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Effect of localized vibrations on the Si surface concentrations of hydrogen or deuterium

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Introduction

Hydrogen is an important technological component for silicon surface passivation during the fabrication of metal oxide semiconductor (MOS) devices. In a recent development [1] deuterium has been substituted for hydrogen in the process of passivation. This resulted in the significant decrease of hot carrier degradation. Being isotopes, deuterium and hydrogen have vitually identical electronic properties. Therefore the significant difference in adatom behavior as observed in [1] must be related to the surface lattice dynamics.

The significant difference in the isotope atoms behavior occurs not only under extreme nonequilibrium conditions but even in the equilibrium properties of isotope atoms on the surface.

This paper deals with the calculations of the concentrations of adatoms H (or D) on the surface of Si which is in thermodynamic equilibrium with hydrogen or deuterium gas.

The description of the equilibrium between the Si surface and the gas of molecules requires the knowledge of both the chemical potential of H(D) on the surface and the chemical potential of H(D) in the gas. Along with the electronic contribution, the chemical potential of the adatom has the vibration contribution which can be found from the lattice dynamics of the impurity atoms on the surface. The chemical potential of H(D) atom in the gas is known from the thermodynamics of two atomic gases. The equality of the chemical potentials of H(D) atoms on the surface and in the gas in the thermodynamic equilibrium enable us to find the surface equilibrium concentrations of the adatoms. The difference of H and D surface concentrations results from the difference of H and D surface localized vibrations. It is shown that the surface concentration of D-adatoms is by 10 to 15 times higher then the concentration of H-adatoms.

1 Dynamics of adatoms on the surface of Si

In order to find the surface localized vibration frequencies, we consider the general form of the equation of the motion for the semiinfinite crystal with some adatoms

$$(\bar{L} - \bar{D})\bar{u} = 0 \tag{1}$$

where $\bar{L}$ represents vibrations of the perfect crystal with the surface and $\bar{D}$ is the perturbation matrix of the adatoms, $\bar{u}$ is the column of the displacement of all the atoms.

For simplicity the nonreconstructed surface (100) of Si with the symmetry of the simple square is considered. We assume that the adatom of the mass $M^{(H)}$ is bound

in the "on–site" configuration to the surface atom of Si with the mass M by the force constant $\gamma\prime$. Restricting ourself by the nearest neighbour approximation for the description of the interaction of the adatoms with the crystal, one can get for the case of the low concentration of the adatoms the following characteristic equation for finding the adatom localized vibration frequency

$$1 - \frac{\gamma'\omega^2}{\omega^2 - \omega_0^2} G(\omega^2) = 0, \tag{2}$$

where $\omega_0^2 = \gamma'/M^{(\mathrm{H})}$, $G(\omega^2)$ is the diagonal element of the Green's function matrix $\bar{G} = \bar{L}^{-1}$.

The Green's function $G(\omega^2)$ can be given in terms of the frequency distribution function of the perfect crystal $g_0(\omega^2)$ [2]

$$\mathrm{Re}G(\omega^2) = \frac{1}{M}\int_0^{\omega_L^2} \frac{g_0(\Omega^2)}{\omega^2 - \Omega^2} d\Omega^2. \tag{3}$$

Here $g_0(\omega^2)$ is normalized to the unity. The quantity ω_L is the maximum frequency of the crystal with the free surface.

Since the localized vibration frequency of the light adatom ω_{loc} satisfying to Eq. (2) is significantly higher than the maximum frequency of the Si phonon spectrum, the main contribution in the integrant at $\omega = \omega_{\mathrm{loc}}$ is given by the high frequency optical vibrations. Because the optical branches have the small dispersion, the important optical part of the distribution function could be approximated by a δ-function

$$g_0(\omega^2) \approx g_0^{\mathrm{opt}}(\omega^2) = \delta(\omega^2 - \omega_L^2). \tag{4}$$

From Eqs. (2)–(4) the algebraic biquadratic equation for the determination of the surface localized frequency ω_{loc} is obtained:

$$1 - \frac{\omega_1^2(\omega^2 + \omega_L^2)}{(\omega^2 - \omega_0^2)\omega^2} = 0. \tag{5}$$

Using the numerical value of the force constant $\gamma\prime$ from [3] $\gamma\prime = 8.8 \times 10^4 \mathrm{din} \cdot \mathrm{cm}^{-1}$, we calculated from Eq. (5) the following localized frequencies of H (or D) stretching localized modes: $\omega_{\mathrm{loc}}^{(\mathrm{H})} = 2.34 \times 10^{14}\,\mathrm{s}^{-1}$ $\omega_{\mathrm{loc}}^{(\mathrm{D})} = 1.70 \times 10^{14}\,\mathrm{s}^{-1}$. We note that $\omega_{\mathrm{loc}}^{(\mathrm{H})} > \omega_{\mathrm{loc}}^{(\mathrm{D})}$. These frequencies differ from the experimental data $\omega_{\mathrm{str}}^{(\mathrm{H})} = 3.96 \times 10^{14}\,\mathrm{s}^{-1}$, $\omega_{\mathrm{str}}^{(\mathrm{D})} = 2.83 \times 10^{14}\,\mathrm{s}^{-1}$ [4]. The discrepancy is apparently the result of our simple approximation.

It is shown in [5] that the account of the next nearest neighbour approximation and of the noncentral forces would result in bending modes obtained along with above mentioned stretching modes. The experimental value of the double degenerate at Γ — point bending mode of H(D) on the surface of Si is $\omega_{\mathrm{bend}}^{(\mathrm{H})} = 1.17 \times 10^{14}\,\mathrm{s}^{-1}$ [4]. Because the bending mode frequency is lower then the stretching mode frequency, stretching modes are the most important for the calculation of the partition function of the system.

2 Chemical potential of H(D) adatom on the surface

In our case of the low surface concentration of adatoms they constitute a two-dimensional dilute solution on the surface of Si. The vibrational part of the partition function of the solution can be given in terms of the frequency distribution function $g(\omega^2)$ of the crystal with adatoms on the surface

$$Z_{\text{cryst}} = \frac{N_{\text{surf}}!}{N_{\text{adatom}}!(N_{\text{surf}} - N_{\text{adatom}})!} \exp\left[-\int_0^{\omega_{\max}^2} d\Omega^2 g(\Omega^2) \ln\left(2\sinh\frac{\hbar\Omega}{2T}\right)\right]. \quad (6)$$

Here N_{surf} is the total number of the dangling bonds on the surface and N_{adatom} is the number of the adatoms. The combinatorial factor represents the possibility of interchanging within both the occupied and empty surface sites. The frequency $\omega_{\max}$ is the maximum frequency of the vibrations for the crystal with adatoms on the surface.

With high accuracy, the total frequency distribution function may be given by

$$g(\omega^2) = 3N_{\text{Si}} g_0(\omega^2) + N_{\text{adatom}} 3\delta(\omega^2 - \omega_{\text{loc}}^2). \quad (7)$$

Substituting (7) in (6) and using the equation for Helmgolz free energy $F = -T \ln Z$ and the equation for the chemical potential of the adatom $\mu_{\text{adatom}} = (\partial F/\partial N_{\text{adatom}})_{TV}$, we get the chemical potential for hydrogen adatom

$$\mu_{\text{surf}}^{(\text{H})} = T \ln n_{\text{adatom}}^{(\text{H})} + 3T \ln\left[2\sinh\frac{\hbar\omega_{\text{loc}}^{(\text{H})}}{2T}\right] + \varepsilon_{\text{H}}, \quad (8)$$

and for deuterium adatom

$$\mu_{\text{surf}}^{(\text{D})} = T \ln n_{\text{adatom}}^{(\text{D})} + 3T \ln\left[2\sinh\frac{\hbar\omega_{\text{loc}}^{(\text{D})}}{2T}\right] + \varepsilon_{\text{D}}. \quad (9)$$

Because binding energies of isotopes are equal, $\varepsilon_{\text{H}} = \varepsilon_{\text{D}}$ and the difference of chemical potentials comes from the difference of localized frequencies $\omega_{\text{loc}}^{(\text{H})} \neq \omega_{\text{loc}}^{(\text{D})}$ only.

3 Chemical potential of H(D)-atoms in the gas phase

The chemical potentials of H and D atoms in the gas is obtained from the conditions of the chemical equilibrium for the reaction of $H_2(D_2)$ dissociation and from the chemical potential of molecule consisting of two identical atoms [6].

$$\mu_{\text{gas}}^{(\text{H})} = \frac{1}{2}[T \ln P_{\text{H}_2} - c_p T \ln T - \zeta_{\text{H}_2} T + \varepsilon_0] \quad (10)$$

and

$$\mu_{\text{gas}}^{(\text{D})} = \frac{1}{2}[T \ln P_{\text{D}_2} - c_p T \ln T - \zeta_{\text{D}_2} T + \varepsilon_0] \quad (11)$$

Here $P_{\text{H}_2}(P_{\text{D}_2})$ is the gas pressure, c_p is the specific capacity at the constant pressure, $\zeta_{\text{H}_2} = \ln[(I_{\text{H}_2}/\hbar^5)(M_{\text{H}_2}/2\pi)^{3/2}]$ and $\zeta_{\text{D}_2} = \ln[(I_{\text{D}_2}/\hbar^5)l(M_{\text{D}_2}/2\pi)^{3/2}]$ are the chemical constants of the hydrogen gas or the deuterium gas, respectively (I_{H_2} and I_{D_2} being the momentum of inertia of the molecules), ε_0 is the binding energy of the molecule in the gas.

4 Concentration of H(D) atoms

The substitution of chemical potentials (8) and (10) for hydrogen or (9) and (11) for deuterium in the condition of thermodynamic equilibrium $\mu_{\text{surf}}^{(\text{H})} = \mu_{\text{gas}}^{(\text{H})}$ and $\mu_{\text{surf}}^{(\text{D})} = \mu_{\text{gas}}^{(\text{D})}$, respectively, allows to find the concentration of hydrogen atoms and the concentration of deuterium atoms on the Si crystal surface in the thermodynamic equilibrium

$$n_{\text{adatom}}^{(\text{H})} = P_{\text{H}_2}^{1/2} T^{c_p/2} \left[\frac{I_{\text{H}_2}}{\hbar^5} \left(\frac{M_{\text{H}_2}}{2\pi} \right)^{3/2} \right]^{1/2} \exp\left[-\frac{\mu_1^{(\text{H})}}{T} \right] \exp\left[-\frac{\frac{1}{2}\varepsilon_0 - \varepsilon_{\text{H}}}{T} \right] \quad (12)$$

$$n_{\text{adatom}}^{(\text{D})} = P_{\text{D}_2}^{1/2} T^{c_p/2} \left[\frac{I_{\text{D}_2}}{\hbar^5} \left(\frac{M_{\text{D}_2}}{2\pi} \right)^{3/2} \right]^{1/2} \exp - \left[\frac{\mu_1^{(\text{D})}}{T} \right] \exp\left[\frac{\frac{1}{2}\varepsilon_0 - \varepsilon_{\text{D}}}{T} \right]. \quad (13)$$

Since the localized frequencies $\omega_{\text{loc}}^{(\text{H})}$ and $\omega_{\text{loc}}^{(\text{D})}$ satisfy the condition $T < \hbar\omega_{\text{loc}}^{(\text{H})}, \hbar\omega_{\text{loc}}^{(\text{D})}$ and $I_{\text{H}_2}/I_{\text{D}_2} = M_{\text{H}_2}/M_{\text{D}_2}$, one can get the following equation for the ratio of the concentrations

$$\frac{n_{\text{surf}}^{(\text{H})}}{n_{\text{surf}}^{(\text{D})}} = \left(\frac{M_{\text{H}_2}}{M_{\text{D}_2}} \right)^{5/4} \exp\left[-\frac{3\hbar[\omega_{\text{loc}}^{(\text{H})} - \omega_{\text{loc}}^{(\text{D})}]}{2T} \right]. \quad (14)$$

It is seen from Eq. (14) that the concentration of deuterium exceeds significantly the concentration of hydrogen due to the difference of both the isotope masses and the localized frequencies.

Using experimental values for localized frequencies of H and D we have found that the ratio of concentrations is about 15 at the typical technological temperature $T = 700$ K.

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